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Field Audit Results with Organic Gas
Standards on Volatile Organic Ambient
Air Samplers Equipped with Tenax GC
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16. ABSTRACT The results from two field audits using Tenax-equipped sampling systems measuring the volatile organic (VOC) concentrations in ambient air are reported. The audited samplers collected the VOC's on Tenax GC® (a porous polymer adsorbent) with the VOC's later thermally desorbed and then analyzed by gas chromatography/mass spectrometry/computer (GC/MS/COMP). Each audit standard, prepared and certified by the National Bureau of Standards (NBS), contained at least four of the following compounds at the low parts per billion (ppb) level in dry N ₂ : C ₆ H ₆ , C ₆ H ₅ CH ₃ , C ₆ H ₅ Br, C ₆ H ₅ Cl, CHCl ₃ , CCl ₄ and C ₂ Cl ₄ . The results of the two audits were consistent and highlight some of the errors associated with sampling for VOC using Tenax GC®. For example, a large negative bias was evident for CCl ₄ even when the sampled volume was less than 10% of the theoretical breakthrough volume. On the other hand, regardless of the volume sampled, a 23-36% positive bias was evident for all but one C ₂ Cl ₄ sample. A positive bias was also evident for both C ₆ H ₆ and C ₆ H ₅ CH ₃ . The negative bias for CCl ₄ indicates that Tenax GC® is not a good medium for sampling this VOC. The positive bias for C ₆ H ₆ , C ₆ H ₅ CH ₃ and C ₂ Cl ₄ suggest that either chemical transformations occurred on Tenax GC® during or after sampling or that Tenax GC® is inherently contaminated with these three VOC's. The agreement between successive sampling runs (repeatability) shows that the audit system itself is a viable means to audit the performance of VOC sampling systems at field sites.		13. TYPE OF REPORT AND PERIOD COVERED
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Field Audit Results with Organic Gas Standards on Volatile Organic Ambient Air Samplers Equipped with Tenax GC

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■ The results from two field audits of Tenax GC equipped sampling systems measuring the volatile organic compound (VOC) concentrations in ambient air are reported. Each audit standard contained at least four of the following compounds at the low parts per billion (ppb) level: C_6H_6 , $C_6H_5CH_3$, C_6H_5Br , C_6H_5Cl , $CHCl_3$, CCl_4 , and C_2H_5Cl . The results of the audits were consistent and highlight some of the errors associated with sampling for VOC's with Tenax. For example, a large negative bias was evident for CCl_4 even when the sampled volume was less than 10% of the published breakthrough volume. However, regardless of the volume sampled, a 23-36% positive bias was evident for all but one C_2H_5Cl sample. A positive bias was also evident for both C_6H_6 and $C_6H_5CH_3$. The agreement between successive audits showed that the system is a viable means to audit the performance of VOC sampling systems at field sites.

Introduction

Tenax GC adsorbent is widely used for collection of volatile organic compounds (VOC's) in ambient air (1, 2). Because of the uncertainties associated with using only a single adsorbent cartridge to collect organics in air (3), EPA/EMSL uses four cartridges to sample simultaneously the same air parcel. However, each cartridge samples at a different flow rate in order to collect air volumes that differ widely (10-80 L). In the past, the performance audits on this latter VOC monitoring system were limited to the analysis of tubes containing Tenax that had been spiked in the laboratory with selected VOC's. This practice was not an entirely adequate quality-assurance procedure because sampling, an integral part of the monitoring system, was not evaluated with this technique.

This situation changed with the recent development of gas cylinders containing stable mixtures of toxic volatile organic compounds at the low parts per billion (ppb) level. These National Bureau of Standards (NBS) materials made on-site field audits of the entire air monitoring system possible (4). This article describes two field audits of ambient air sampling systems using Tenax that were conducted with these NBS VOC reference standards. Since the cylinders contained several aromatic and aliphatic hydrocarbons/halocarbons at 1-12 ppb, they were used without sample dilution. These audits provided an assessment of the accuracy and precision of an EPA-operated ambient air sampler that used Tenax to collect VOC's from air. However, they also provided information on the capabilities of Tenax under field sampling conditions that will be useful for those considering the use of Tenax for VOC's.

Experimental Section

The audit materials, contained in 150-ft³ aluminum cylinders with a balance gas of N_2 , were gravimetrically prepared by the NBS and then analyzed by at least two different analytical methods. The single standard used in the first field audit (1983) contained the following mixture of aliphatic and aromatic compounds: $CHCl_3$ (3.8 ppb), C_2Cl_4 (12.4 ppb), CCl_4 (7.7 ppb), C_6H_6 (8.7 ppb), and

$C_6H_5CH_3$ (6.4 ppb). The two standards used in the second field audit (1985) contained either four aromatics or four aliphatics. The cylinder with the aromatics contained C_6H_6 (0.93 ppb), $C_6H_5CH_3$ (0.88 ppb), C_6H_5Cl (1.42 ppb), and C_6H_5Br (1.22 ppb). The cylinder with the aliphatics contained $CHCl_3$ (1.08 ppb), C_2Cl_4 (1.85 ppb), CCl_4 (1.15 ppb), and C_2H_5Cl (0.90 ppb). The preparation and analysis of low ppb VOC standards by NBS has been reported previously (5). The audit standards were analyzed by NBS before and after the performance evaluation to verify stability of the components during the audit. The reanalysis showed that the concentrations were unchanged. The estimated uncertainty in the certified concentrations is less than 0.08 ppb for all compounds. The gravimetrically determined concentrations (ppb) of VOC's in the cylinder were converted into nanograms per liter units with the ideal gas equation ($PV = nRT$). The amounts (ng) of VOC's delivered to the Tenax cartridges were then calculated from the volume of gas sampled.

At both field sites the mass flow controllers used in the VOC samplers were audited with laminar flow elements certified by the NBS. At both sites the gas flow from the cylinder was controlled with a 350 CGA reducing adapter and needle valve. The gas passed from the cylinder to the sampler through 39 cm of 3 mm o.d., 316 SS tubing that was connected to the sampler with a Sovirel fitting equipped with Teflon gaskets. Before the field audits began, the gas delivery system was checked for losses by passing SO_2 at the low ppb level through it and measuring the outlet concentration. No losses were found.

Three audit runs were done in the 1983 audit with run times of 30, 30, and 60 min. In each run, two samplers were audited with one sampler operating at 50 cm³/min and the other at 95 cm³/min. Four, 3-h audit runs were done in the 1985 audit, two from the aromatic cylinder and two from the aliphatic cylinder. In each run four samplers were audited simultaneously with the samplers operating at one of the following flows: 55, 110, 220, and 440 cm³/min. Each sampler contained 1.2 g of Tenax in a glass (1983 audit) or 316 SS (1985 audit) tube approximately 15 mm (o.d.) $\times$ 100 mm long.

At the completion of the audit, the samples were returned to the laboratory by common carrier where they were analyzed by GC/MS/COMP in the same manner as the actual air samples. The GC/MS calibration standards were prepared in a glass flask equipped with a resealable valve for withdrawal of aliquots by syringe. Small amounts of pure VOC's were introduced into the flask where they were volatilized with heat and agitation to provide a stable, uniform gas standard (6). The GC/MS was calibrated by direct injections of this gaseous VOC standard into the "splitless" injection port with a gas-tight microsyringe. The Tenax cartridges were analyzed by thermal desorption at 270 °C for 8 min into the GC/MS using a NuTech Model 320 thermal desorption unit (7).

The Tenax used in the audit was cleaned up by Soxhlet extraction with methanol and pentane (8 h each) and, after removal of the solvent, was also thermally desorbed at 270 °C for 4 h.

Table I. 1983 Aliphatic/Aromatic Audit Results^a

run	vol, L	compd ^b	amount, ng		bias, %
			delivered	reported	
1	1.5	C ₆ H ₆	43.4	49.4	13.8
		C ₆ H ₅ CH ₃	37.6	48.1	27.9
		CHCl ₃	28.9	31.5	9.0
		C ₂ Cl ₄	131	136	3.8
		CCl ₄	75.6	54.2	-28.3
	2.85	C ₆ H ₆	82.4	96.1	16.6
		C ₆ H ₅ CH ₃	71.4	92.5	29.6
		CHCl ₃	54.9	58.0	5.6
		C ₂ Cl ₄	249	271	8.8
		CCl ₄	144	102	-29.2
2	1.5	C ₆ H ₆	43.4	55.8	28.6
		C ₆ H ₅ CH ₃	37.6	58.9	56.6
		CHCl ₃	28.9	35.4	22.5
		C ₂ Cl ₄	131	151	15.3
		CCl ₄	75.6	57.1	-24.5
	2.85	C ₆ H ₆	82.4	98.7	19.8
		C ₆ H ₅ CH ₃	71.4	98.6	38.1
		CHCl ₃	54.9	60.4	10.0
		C ₂ Cl ₄	249	291	16.9
		CCl ₄	144	103	-28.5
3	3.0	C ₆ H ₆	87.5	110	25.7
		C ₆ H ₅ CH ₃	75.9	124	63.4
		CHCl ₃	56.9	63.4	11.4
		C ₂ Cl ₄	265	308	16.2
		CCl ₄	152	114	-25.0
	5.7	C ₆ H ₆	166	185	11.4
		C ₆ H ₅ CH ₃	144	185	28.5
		CHCl ₃	108	108	0.0
		C ₂ Cl ₄	503	577	14.7
		CCl ₄	290	194	-33.1

^a C₆H₆ and C₆H₅CH₃ results corrected for field blanks of 9 and 11 ng/cartridge, respectively. ^b Breakthrough volumes (L) are C₆H₆ (50), C₆H₅CH₃ (240), CHCl₃ (20), C₂Cl₄ (200), and CCl₄ (20).

Results and Discussion

All sample flows were within 2% of the flow audit standards. Table I presents the organic audit results from the 1983 audit; Tables II and III present the results for the 1985 aromatic and aliphatic audits, respectively. (C₂H₃Cl is not reported because its breakthrough volume was exceeded in all samples.) Breakthrough volumes cited are from Krost (8). In these tables, the percent bias was calculated as

$$\% \text{ bias} = \frac{\text{ng reported} - \text{ng delivered}}{\text{ng delivered}} \times 100$$

In reviewing these results, bear in mind that they are for a Tenax-equipped sampler sampling a clean, dry N₂ stream containing only a few organics—an ideal sampling situation. Therefore, they cannot be applied directly to such a system sampling ambient air.

Although major differences existed between the two audits, the results are surprisingly similar. Some of the major differences between the audits were as follows: (1) the VOC concentrations in the 1983 audit were 3–12 times higher than those in the 1985 audit; (2) an aromatic/aliphatic mixture was used in the 1983 audit whereas separate aliphatic and aromatic mixtures were used in the 1985 audit; (3) the sampled volumes in the 1983 audit (1.5–5.7 L) were smaller than those in the 1985 audit (9.6–78.9 L). Despite these differences, the following similarities are apparent:

(1) C₆H₆ and C₆H₅CH₃. A positive bias is evident for all C₆H₅CH₃ results and for C₆H₆ for all but the two highest sampled volumes. (These latter volumes are 27–29 L above the published breakthrough volume of 50 L for benzene.) These results suggest that these compounds were either released directly from the Tenax or formed chemically

Table II. 1985 Aromatic Audit Results^a

run	vol, L	compd ^b	amount, ng		bias, %
			delivered	reported	
1	10.1	C ₆ H ₆	30	62	107
		C ₆ H ₅ CH ₃	34	49	44
		C ₆ H ₅ Cl	67	NR ^c	
		C ₆ H ₅ Br	80	91	13.8
		C ₆ H ₆	61	65	6.6
	20.3	C ₆ H ₅ CH ₃	68	81	19.1
		C ₆ H ₅ Cl	135	NR	
		C ₆ H ₅ Br	162	11	-93.2
		C ₆ H ₆	119	122	2.5
		C ₆ H ₅ CH ₃	133	148	11.3
2	39.4	C ₆ H ₅ Cl	262	NR	
		C ₆ H ₅ Br	314	369	17.5
		C ₆ H ₆	238	224	-5.9
		C ₆ H ₅ CH ₃	266	304	14.3
		C ₆ H ₅ Cl	524	513	-2.1
	78.9	C ₆ H ₅ Br	628	634	1.0
		C ₆ H ₆	29	46	58.6
		C ₆ H ₅ CH ₃	33	48	45.5
		C ₆ H ₅ Cl	64	NR	
		C ₆ H ₅ Br	77	91	18.2
3	9.6	C ₆ H ₆	59	73	23.7
		C ₆ H ₅ CH ₃	66	92	39.4
		C ₆ H ₅ Cl	131	NR	
		C ₆ H ₅ Br	157	184	17.2
		C ₆ H ₆	117	138	17.9
	19.3	C ₆ H ₅ CH ₃	131	164	25.2
		C ₆ H ₅ Cl	258	281	8.9
		C ₆ H ₅ Br	309	348	12.6
		C ₆ H ₆	236	233	-1.3
		C ₆ H ₅ CH ₃	264	321	21.6
4	38.1	C ₆ H ₅ Cl	519	538	3.7
		C ₆ H ₅ Br	622	680	9.3
		C ₆ H ₆	236	233	-1.3
		C ₆ H ₅ CH ₃	264	321	21.6
		C ₆ H ₅ Cl	519	538	3.7
	76.8	C ₆ H ₅ Br	622	680	9.3
		C ₆ H ₆	236	233	-1.3
		C ₆ H ₅ CH ₃	264	321	21.6
		C ₆ H ₅ Cl	519	538	3.7
		C ₆ H ₅ Br	622	680	9.3

^a C₆H₆ and C₆H₅CH₃ results corrected for field blanks of 33 and 10 ng/cartridge, respectively. ^b Breakthrough volumes (L) are C₆H₆ (50), C₆H₅CH₃ (240), C₆H₅Cl (470), and C₆H₅Br (1100). ^c Not reported.

Table III. 1985 Aliphatic Audit Results

run	vol, L	compd ^a	amount, ng		bias, %
			delivered	reported	
1	10.0	CHCl ₃	53	68	28.3
		CCl ₄	74	57	-23.0
		C ₂ Cl ₄	125	171	36.8
		CHCl ₃	105	119	13.3
		CCl ₄	147	96	-34.7
	38.5	C ₂ Cl ₄	249	324	30.1
		CHCl ₃	204	149	-27.0
		CCl ₄	286	143	-50.0
		C ₂ Cl ₄	484	606	25.2
		CHCl ₃	404	177	-56.2
2	76.4	CCl ₄	568	175	-69.2
		C ₂ Cl ₄	961	1184	23.2
		CHCl ₃	53	72	35.8
		CCl ₄	75	54	-28.0
		C ₂ Cl ₄	127	167	31.5
	20.0	CHCl ₃	106	123	16.0
		CCl ₄	149	85	-43.0
		C ₂ Cl ₄	252	331	31.3
		CHCl ₃	206	141	-31.6
		CCl ₄	289	81	-72.0
3	38.9	C ₂ Cl ₄	489	607	24.1
		CHCl ₃	409	153	-62.6
		CCl ₄	575	134	-76.7
		C ₂ Cl ₄	972	NR ^b	
		CHCl ₃	409	153	-62.6
	77.3	CCl ₄	575	134	-76.7
		C ₂ Cl ₄	972	NR ^b	
		CHCl ₃	409	153	-62.6
		CCl ₄	575	134	-76.7
		C ₂ Cl ₄	972	NR ^b	

^a Breakthrough volumes (L) are CHCl₃ (20), CCl₄ (20), and C₂Cl₄ (200). ^b Not reported.

during or after sampling. When one considers the extent of the apparent contamination, the overall agreement between runs is good.

The standard deviations of the percent bias for benzene and toluene were 10.9 and 15.4, respectively. On the basis of our laboratory's experience, the estimated precision of the analysis of Tenax field samples for many compounds is only $\pm 30\%$.

The two highest percent bias values for benzene were rejected at the 5% significance level with the Dixon ratio test for outliers and were not included in the calculation of standard deviation.

(2) C_6H_5Cl . This compound was detected only after the Tenax had been exposed to a large quantity of C_6H_5Cl . Although the amount of data is limited, the results achieved for percent bias are in close agreement (-2.1% , 8.9% , and 3.7%).

(3) C_6H_5Br . A positive bias is evident in the results, but overall precision and accuracy were above expectations with a mean and standard deviation of 12.8 and 6.1, respectively. The lowest percent bias value was rejected with the Dixon ratio test for outliers.

(4) $CHCl_3$. At low volumes a positive bias was evident, but as the breakthrough volume (20 L) was approached, the collection efficiency apparently decreased sharply. (It would not be surprising if breakthrough occurs at even lower volumes when complex air matrices are sampled.)

(5) CCl_4 . A negative bias was found even when the sampled volume was less than 10% of the breakthrough volume (20 L). This would indicate that Tenax is not suitable for quantitatively sampling for CCl_4 . This negative bias was also found by the NBS as a result of experiments to determine the recovery efficiencies of certain VOC's loaded on Tenax (9).

(6) C_2Cl_4 . A positive bias was found in all cases where C_2Cl_4 was detected.

Conclusions

Field audit results on Tenax-equipped samplers identified some problems with these type of samplers. The results obtained in the audits showed that successful on-site field evaluations of air monitoring systems using Tenax can be conducted with gas cylinders containing VOC's. By use of cylinders certified or analyzed by the NBS, traceability to a common reference can be established. Ambient air monitoring systems using other collection techniques should also be amenable to this audit approach.

Because actual atmospheric sampling conditions, pollutants, and pollutant concentrations cannot be exactly duplicated, this audit approach does not assess the performance of a VOC sampling system under conditions encountered during actual sampling. It does provide information, however, that can indicate if the sampling/analytical measurement system is operating properly and within expectations.

Registry No. C_6H_6 , 71-43-2; $C_6H_5CH_3$, 108-88-3; C_6H_5Br , 108-86-1; C_6H_5Cl , 108-90-7; $CHCl_3$, 67-66-3; CCl_4 , 56-23-5; C_2Cl_4 , 127-18-4; Tenax GC, 24938-68-9.

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